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Progress Report

to the

National Aeronautics and Space Administration

Sulfur mass loading of the atmosphere from volcanic eruptions : Calibration
of the Ice Core Record on Basis of Sulfate Aerosol Deposition in Polar

Regions from the 1982 El Chichon Eruption

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Introduction

Major volcanic eruptions disperse large quantities of sulfur compounds throughout the Earth's atmosphere. The sulfuric acid aerosols resulting from such eruptions are scavenged by snow within the polar regions and appear in polar ice cores as elevated acidity layers. Glaciochemical studies of ice cores can thus provide a record of past volcanism, as well as the means for understanding the fate of volcanic sulfur in the atmosphere. The primary objectives of this project are to study the chemistry and physical properties of volcanic fallout in a Greenland Ice Core, in order to evaluate the impact of the volcanic gases on the atmospheric chemistry and the total atmospheric mass of volcanic aerosols emitted by major volcanic eruptions. We propose to compare the ice core record to other atmospheric records performed during the last 10 years to investigate transport and deposition of volcanic materials.

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This study is a collaborative project between NASA, Goddard Space Flight Center (Dr. Louis S. Walter) and the University of Rhode Island (Dr. Haraldur Sigurdsson and Paolo Laj).

Methodology

Our samples originate from an ice core drilled by the polar Ice Coring Office in July 1985 at Site A in Central Greenland (70° 45' N. 35° 57' W, 3145 m.a.s.l.), using an electromechanical 4-inch drill. The core is 95.5 m long and 10 cm diameter. It is in moderately good condition with some sections greatly fractured especially at the top and the close-off portions of the core. Samples were taken from the side of the core for density measurements and the core sections were then sealed in polyethylene bags and stored in insulated boxes at the SUNY ice core facility at Buffalo N.Y., awaiting for analysis.

A conductivity profile of the entire core was performed using a solid conductivity technique developed at the Glacier Research Group of the University of New Hampshire in order to detect high-acidity volcanic layers. We then sampled the high conductivity layers, presumably associated with volcanic acid deposits, as well as the adjacent parts of the core corresponding to periods of 3 to 4 years before and after each volcanic event. Eight different core sections were sampled, corresponding to a total length of 29.5 m of core. Each section was then sampled every 4 to 7 cm (about 2 months) using ice-clean procedures. All tools in contact with the ice core samples were extensively cleaned and tested to ensure that the samples were processed without contamination, and all laboratory handling of the ice core before analysis was conducted in a cold room (-20°C). The outer portion of the core was removed using a circular saw with a stainless steel blade, which was tested for contamination before and after each core sectioning. Samples from sections below the close-off depth (75 m) were washed with Milli-Q water before melting. We analyzed a total of 400 samples and 91 blanks, as well as duplicate analyses of 40 of these samples for major anions and cations, hydrogen peroxide and microparticles.

Anion (Cl^- , NO_3^- , SO_4^{2-}) and cation (Na^+ , NH_4^+ , Mg^{2+} , K^+ , Ca^{2+})

analyses were performed using a Dionex™ Model 2010 ion chromatograph with AS-4 column and 0.0021 M NaHCO₃/0.0017 M Na₂CO₃ eluent for anion and CS-2 and preconcentration columns and 18 mg HCl/1.4 mg DAP eluent for cation, and a computer driven autosampler. Sample concentrations were determined using a standardization curve and a standard analysis was performed every 20 samples. The precision of the method is on the order of 10% of the sample concentration.

The H₂O₂ measurements were performed using a fluorimetric method based on the reaction of H₂O₂ with horseradish peroxidase and p-hydroxyphenylacetic acid (POPHA). The resulting reaction forms the fluorescent dimer of POPHA which can be detected using a conventional fluorescence detection technique. The precision of the method is on the order of 7% of the sample concentration.

The particle analyses were conducted using an Elzone particle counter with a 30µm orifice tube. Milli-Q water and concentrated electrolyte were filtered through 0.15 µm Millipore filters and tested for particles before sample analyses. Samples were diluted to a 4% electrolyte solution. The particle size distribution covers the range of 0.4 to 14 µm.

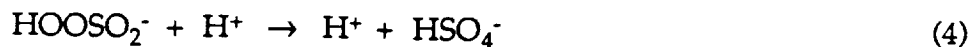
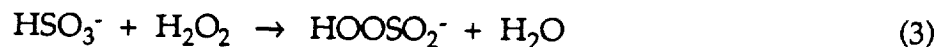
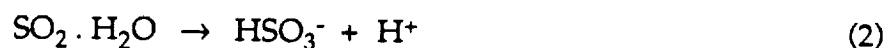
Our record covers both volcanic and non-volcanic periods from the early seventeenth century until 1985 and therefore provides a valuable record of the changes which affected the Arctic atmosphere during this time. A preliminary depth-age relationship was carried out using density measurements, snow accumulation rates and comparisons with another core drilled at Site A (E. Mosley-Thompson, personal communication). Depth, corresponding age and origin of the volcanic signal in the sampled sections of the core are summarized in Table 1.

Preliminary results

The volcanic deposits in the Greenland ice core are characterized by a significant enhancement in non-sea salt SO₄²⁻ concentrations, with enrichment up to twenty times the background level in the case of the Laki 1783 eruption. Because of the volcanic gas dispersion in the atmosphere,

deposition on the ice sheet is occurring during periods of time ranging from 1 to 12 months as in the case of the 1815 Tambora eruption. In some cases such as the 1875 Askja eruption or the 1912 Katmai eruption, the sulfate peak is associated with a chlorine peak. This is not the case however for the 1815 Tambora deposits although petrologic studies have shown a very large chlorine emission. Such emissions of huge quantities of sulfur and chlorinated species into the atmosphere is very likely to modify the atmospheric chemical equilibrium by destroying or producing important chemical compounds. These changes are recorded in the ice core record and we found evidence of modifications affecting both the H_2O_2 and the NO_3 record.

Seasonal variations in the Cl/Na ratio in polar snow have been observed and have been used in this study to identify summer periods (Figure 1). Both sulfate and hydrogen peroxide exhibit seasonal variations in polar snow with peaks in the summer. At depth, the seasonal variation in the peroxide profile are less clear (Figure 1) due to diffusion of the peroxide in the ice. For all of the volcanic events, a distinct deviation from the expected seasonal peroxide profile is evident and very strongly correlated with increased excess sulfate attributed to the volcanic events. This pattern is observed both for high latitude, (Laki 1783, Hekla 1947 and Katmai 1912) and low latitude (Tambora 1815), eruptions, although these eruptions were chemically different and took place at different times of the year. The depletion of H_2O_2 with excess sulfate suggests that part of the volcanic sulfur was present as SO_2 over Greenland at the time precipitation was forming, and may indicate that reaction occurred between H_2O_2 and SO_2 in the supercooled water film at the surface of ice crystals according to the following mechanism:



It is premature at this point to rule out the possibility of H_2O_2 destruction catalyzed by volcanic dust particles. However, all these eruptions show the same pattern despite differences in the amount of dust which would be reaching Greenland. Furthermore, atmospheric simulation of HO_2 concentrations after the El Chichon eruption shows that HO_2 concentrations changes in the volcanic plume are not significant enough to account for the H_2O_2 depletion. Examination of the Cl/Na ratio establishes that the acid deposition took place for a period of one year or more following the Tambora and Katmai events. H_2O_2 decreases, however, are only observed during summer. Thus, the SO_2 - H_2O_2 reaction does not appear to take place at an efficient rate during the winter. In the Laki layer, the extensive SO_2 emission may have completely depleted peroxide in the precipitation. Some changes also seem to be affecting the NO_3 record after the Laki eruption although the NO_3 depletion is much less significant than the H_2O_2 one.

Our analyses also provide useful information concerning the particles deposition into the Greenland ice. Increase in the particle concentration as well as in the mode of the size distribution have been detected following the Laki eruption, providing the first evidence of volcanic silicate or tephra particles deposited in the Greenland area (Figure 2). An interesting feature is that the sulfate and tephra particle depositions do not take place at the same time, leading to the conclusion that the atmospheric processes involved in the deposition and the advection are different depending on the chemical reactivity and/or the structure of the atmospheric constituent.

The chemical record of the Arctic atmosphere also provide a lot of information on the atmospheric changes which occurred in the Northern Hemisphere since the preindustrial time. A good example is the increase in the NO_3 concentrations since the 1950's due to the anthropogenic activities (Figure 3) but other important atmospheric chemical species may have been affected as well.

Further Work in Progress

The chemical composition of the particles and the volcanic glass shards deposited in the snow, has to be investigated and will provide useful

information on the particle source areas and a definite answer regarding the volcanic origin of the sulfate increase. This will be performed using the facilities of the Massachusetts Institute of Technology equipped with a scanning electron microscope and an EDAX analyzer.

Further work is needed to investigate the chemical modifications affecting the atmosphere following large volcanic eruptions especially changes related to the nitrate and the ammonium cycles. The Site A ice core also provide a 10 year continuous record (1975-1985) of the Arctic atmosphere composition. This record, which then includes both chemical data and particle analyses, can be compared to the in situ measurements performed in the Arctic region and the remote sensing record. This is especially interesting in the case of the recent volcanic events which have been monitored by remote sensing and which are detected as elevated sulfate layers in the core, like the 1979 Hekla eruption, the 1980 Mt St Helens eruption and perhaps the 1982 El Chichon eruption, although the sulfate signal from this eruption does not appear to be significantly above the background level. Such comparisons are an important step to understand the deposition mechanisms of volcanic material into the polar ice and the air exchanges between stratosphere and troposphere which will then be applied to the glacial record of past volcanism.

The behavior of the chlorinated chemical species emitted during volcanic eruptions is still an open question. Our preliminary results indicate that volcanic HCl can be dispersed in the atmosphere at least on a regional scale and therefore has the potential of affecting the ozone cycle but such hypothesis has to be further quantify.

Finally, the chemical and particulate record during non volcanic periods has to be investigated. A clear understanding of the parameters involved in the production and the deposition of chemical species and dust particles into the ice will permit to better quantify the human impact on the Arctic atmosphere.

Conclusions

The ice core record thus provide very useful information on the atmospheric composition during volcanic and non-volcanic periods. The Site

A record covers both preindustrial and present times and can be used to investigate both production and deposition of chemical species and particulate matter in the the Arctic area. This is particularly interesting in the case of the recent volcanic events which have been detected in the core and also monitored by both remote sensing and in situ measurements. A comparison between these different records will lead to a better understanding of the atmospheric and chemical processes involved in the dispersion and the deposition of volcanic material. Such results can then be applied to the record of past volcanism which still is mostly provided by the polar ice cores. These problems will be tackled in the second half of our funding period during this grant.

Sampled Sections	Estimated age interval	Volcanic events
0 m - 6.2 m	1985-1975	El Chichon 1982, Mt St Helens 1980, Hekla 1979, Alaid 1980
10.8 m - 14 m	1965-1958	Agung 1963
21 m - 24.4 m	1949-1942	Hekla, 1947
35 m - 38 m	1915-1906	Katmai 1912
48.5 m - 50.7 m	1880-1874	Askja 1875
69 m - 72 m	1820-1810	Tambora 1815
79 m - 82 m	1794-1784	Laki 1783
93.5 m - 95.5 m	1735-1730	

Table 1: Sampled and analyzed sections of the Site A, Greenland Ice Core

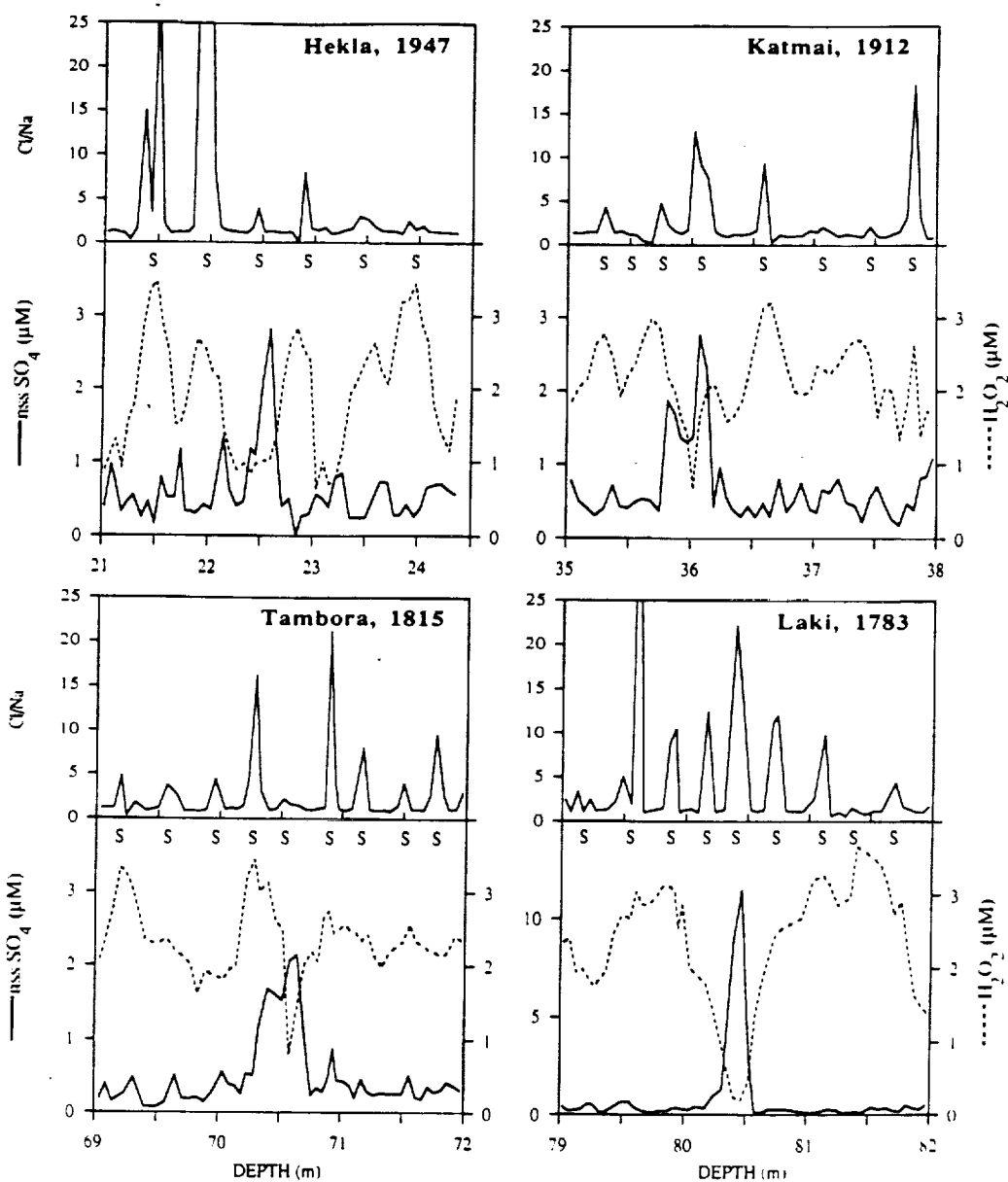


Figure 1: Variation in non-sea salt SO_4^{2-} concentration (solid line) and H_2O_2 concentration (broken line) as a function of depth in four sections of the Site A, Greenland ice core. summer periods, based on variations of the Cl/Na ratio, are identified by "S". Note the sharp decline in peroxide concentration in the ice core at the time of the volcanic events, especially in the case of Laki 1783 and Tambora 1815 eruptions.

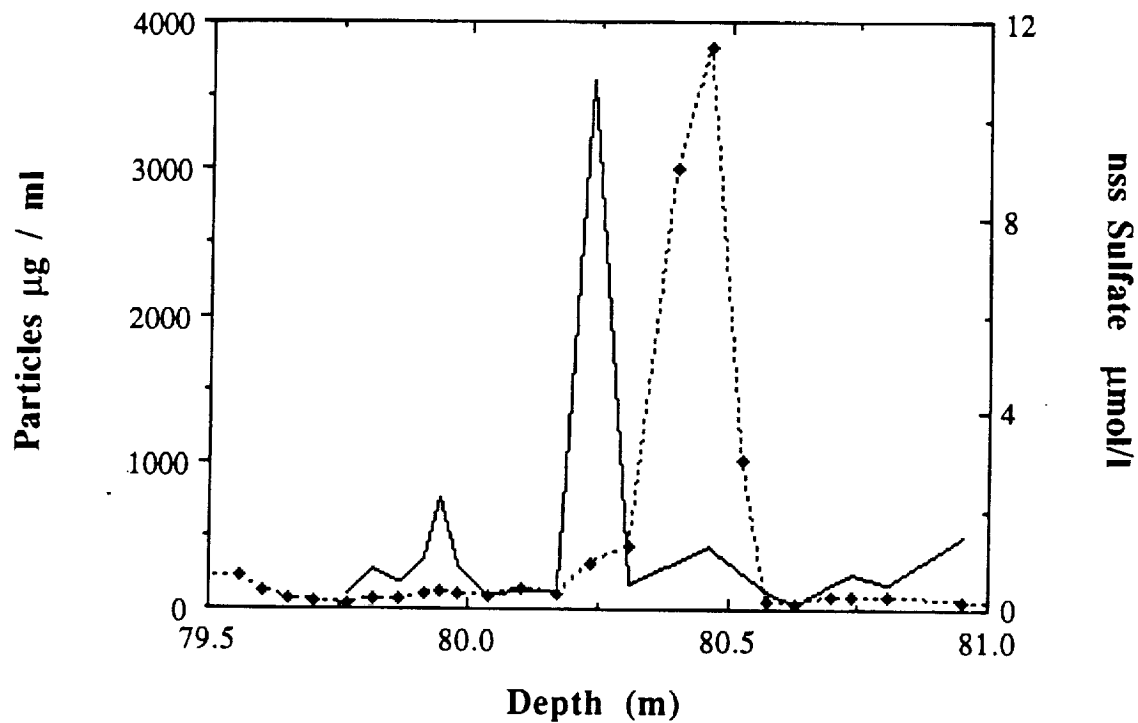


Figure 2: Non-sea salt Sulfate (dashed line) and tephra or silicate particle mass (plain line) in the Greenland Site A, ice core, showing the volcanic acid and volcanic tephra particle fallout peaks from the 1783 Laki eruption in Iceland. Note the time lag between acidity and tephra particle fallout.

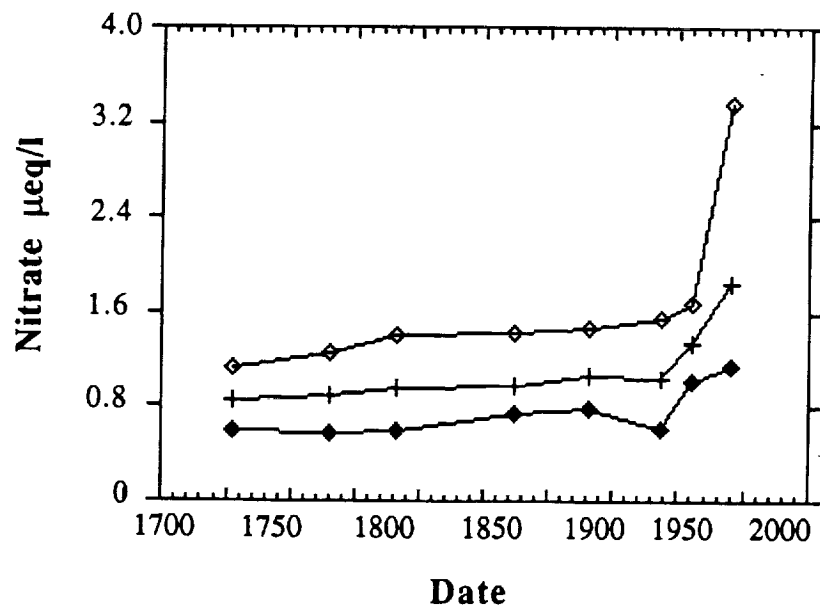


Figure 3: Average nitrate concentration for spring (\diamond), autumn (\blacklozenge) and yearly ($+$) periods in the Greenland Site A ice core, spanning the period from 1725 to 1980 AD. Note the marked increase in the twentieth century due to anthropogenic sources.